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Artigo de Pesquisa

# Tannin Extraction from the Bark of *Pinus oocarpa* var. *oocarpa* with Sodium Carbonate and Sodium Bisulfite

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#### ABSTRACT

Tannin Extraction from the bark of *Pinus oocarpa* var. *oocarpa* with sodium carbonate and sodium bisulfite. The objective of this study was to evaluate the tannin extraction potential taken from the bark of *Pinus oocarpa* var. *oocarpa*. Nine treatments were performed; the bark was submitted to extraction using water and water containing different concentrations of sodium carbonate and sodium bisulfite. The mixture was kept under reflux for two hours. The extracted contents, the polyphenol found in the extracts (Stiasny number), the tannin yield, the non-tannin yield and the tannin reactivity through UV method were all determined. The results have revealed that it is possible to obtain high tannin content (approximately 39%) from the bark of *Pinus oocarpa* var. *oocarpa* by using water extraction when coupled with the addition of salt. The treatment having (8%) of sodium carbonate provided a greater yield of condensed tannins, underlining the importance of utilizing this salt with this concentration during the extraction process. However, the extracts must be evaluated according to other important wood-gluing properties, such as viscosity and gel time.

Keywords: Pinus oocarpa, bark, tannins.

# Extração de Taninos da Casca de *Pinus oocarpa* var. *oocarpa* com Carbonato de Sódio e Bissulfito de Sódio

#### **RESUMO**

O objetivo deste estudo foi avaliar o potencial de extração de tanino retirado da casca de *Pinus oocarpa* var. *oocarpa*. Nove tratamentos foram realizados e a casca foi submetida à extração usando água e contendo diferentes concentrações de carbonato de sódio e bissulfito de sódio. A mistura foi mantida sobre refluxo, durante duas horas. Do conteúdo extraído, os polifenóis presentes nos extratos(número Stiasny), o teor de tanino, o teor de tanino e não reatividade de taninos pelo método UV foram determinados. Os resultados revelaram que é possível obter alto teor de tanino (aproximadamente 39%) da casca de Pinus oocarpa var. oocarpa, usando a extração da água quando combinada com a adição de sal. O tratamento com (8%) de carbonato de sódio proporcionou a maior produção de taninos condensados, evidenciando a importância de se utilizar este sal com esta concentração durante o processo de extração. No entanto, os extratos devem ser avaliados de acordo com outras importantes propriedades de colagem de madeira, tais como a viscosidade e o tempo de formação de gel.

Palavras-chave: Pinus oocarpa, casca, taninos.

### 1. INTRODUCTION

Tannins are comprised in a group of substances occurring in various higher plant species, having the capacity to transform animal skins and hides into leather. The process is achieved associating the hydroxyl groups of tannins with the peptide bonds of amino acids present in animal protein, known as collagen (Haslam, 1966). Besides the tanning action, tannin solutions have other purposes, including: manufacturing of tiles and floors; assisting the drilling of oil wells; acting as dispersants and flocculants, amongst others (Poser & Gosman, 1990).

According to Pizzi (1983), the term "tannin" has been frequently adopted to define two different groups of chemical compounds of phenolic nature: hydrolysable tannins and condensed tannins. Hydrolysable tannins can be considered polyesters derived from glucose, these can be classified into two categories: a) gallotannins, which release gallic acid and its derivatives when submitted to acid hydrolysis; and b) ellagitannins, which upon hydrolysis release ellagic acid and valonic acid - ellagic acid being the most significant (Clifford & Scalbert, 2000).

Condensed tannins consist of flavonoid units, known as flavan-3-ols (catechins) and flavan-3,4-diols (leucoantocyanidins) (Pizzi, 1983; Schofield et al., 2001). These present various degrees of condensation, do not suffer hydrolysis and precipitate with formaldehyde and hydrochloric acid, according to the Stiasny reaction (Roffael & Dix, 1994). The condensed tannins are most commonly presented as polymers, with an average degree of condensation ranging from 4 to 12 flavonoid units.

Plants have a natural ability to defend themselves against their natural enemies - this defensive capability is linked to the presence of tannins. Such compounds are responsible for the astringency of many fruits and plants, due, in part, to the complexes formed between tannins and proteins, the basis for some of their biological properties including the control of insects, fungi and bacteria (Scalbert, 1992; Luck et al., 1994; Aerts et al., 1999). Concerned with the action of hydrolysable tannins in herbivores, Guimarães-Beelen et al. (2006) reported that said compounds may be involved in the animal's digestive process, hampering it, due to the complexes formed between tannins and certain proteins involved with the production of digestive enzymes.

Tannins can range between 2 and 40% of the dry bark of many species (Hergert, 1989). Such values may render the product economically viable for industrial utilization when the range of possible applications for tannins is considered. Tannins are most commonly obtained from the wood and bark of certain deciduous trees, since, except for their bark, coniferous trees possess only a small amount of tannins. The bark of Picea abies can contain up to 15% tannin. Some mangrove species can possess values of up to 35%, and, in the case of the Quebracho tree (Schinopsis balance Engl.), the tannin content varies between 30 and 35% (Roffael & Dix, 1994). Weismann & Ayla (1980), working with the conifer bark extracted, using hot water, ascertained levels between 25 and 30% of extractives, which possessed high levels of tannins.

In some species of pine, polyphenols may appear in the form of phlobaphens, this form being highly condensed and insoluble in water. In literature, there are reports indicating the bark can also contain large amounts of non-phenolic compounds (Dix & Marutzky, 1982). According to Roux et al. (1975), when extracting the bark with weak alkaline solutions or in the presence of sulfite and bisulfite, the pyran rings of polyphenols are partly cleaved with the formation and deposition of carboxylic groups and sulfonic acids. Therefore, the solubility of phlobaphens increases considerably.

Tannins are also used to substitute for synthetic resins thanks to its characteristic to precipitate with formaldehyde, forming a polymer of rigid structure (Gonçalves & Lelis, 2000). The reaction of tannins with formaldehyde represents the basis for its role as an adhesive, forming polycondensates of high molecular weight (Roffael & Dix, 1994). The reaction of polyphenols with formaldehyde enables its use in the manufacture of wood panels under normal gluing and pressing conditions (Prasetya & Roffael, 1991).

Tannins from the bark of the black wattle and the quebracho tree are considered to be the most important condensed tannins produced in industry. In Brazil, work involving tannins, including wood gluing, was initiated in the late 1970's and early 1980's (Coppens et al., 1980; Santana et al., 1981). However, only recently has this theme come to prominence again (Gonçalves, 2000; Tostes, 2003; Mori et al., 1999, 2000).

Among the botanical species, the genus Pinus possesses great potential for the extraction of tannins, since it covers much of the reforestation areas in Brazil. According to SBS (Sociedade..., 2007), approximately 3,000 companies in Brazil use pinewood in their productive processes, concentrating on the following products: sawn wood, cellulose, and paper and panels (plywood, MDF and OSB). Pine bark is a residue for the majority of the wood industries, presenting an environmental and economic challenge upon disposal (Borges et al., 1993).

The international market for tannin extracts of vegetable origin produces about 160,000 tons per annum (TPA), approximately 100,000 TPA originating from acacia plantations; the remainder is sourced from other species, including: Castanheira (Italian), Quebracho (Argentinean) and Tara (Peruvian). The TANAC S/A company, located in southern Brazil, is the largest vegetable extract producer in the world, having the capacity to produce 32,000 TPA of products. Another Brazilian company, SETA, has two factories having the capacity to produce 27,000 TPA. Production in Brazil is similar to numerous African countries, where the favorable climate allows for acacia forests. TANAC occupies 26,000 ha, cultivated close to the port in Rio Grande, in the State of Rio Grande do Sul, from where it is exported as residual firewood to Japan (Química, 2004).

In Brazil, work involving tannins from pine is still incipient. Perhaps the first study to address this topic was Ferreira (2004), having worked with eight pine species planted in Brazil. The author demonstrated that Pinus oocarpa and Pinus caribaea presented potential to supply tannins for wood gluing. A possible alternative for the extracted bark would be the extraction of tannins to produce wood glue, and the residue obtained after extraction could be burned for energy generation.

#### 1.1. Objective

The objective of this study was to evaluate the tannin extraction from the bark of Pinus oocarpa

var. oocarpa tree using water and water containing sodium carbonate and sodium bisulfite, aiming for partial or complete adoption as an adhesive in the manufacturing of wood panels.

### 2. MATERIALS AND METHODS

### 2.1. Material

Bark of Pinus oocarpa was collected from Fazenda Monte Alegre, Duratex, located in Agudos, Sao Paulo. All bark had been randomly chosen from five trees in two plots, with diameter at breast height (DBH) ranging between 15 and 40 cm. Consequently, the trees were marked and their barks removed using a machete, and, as a standard, the removal of bark began at DBH all the way to the base of the standing trees. The material was then sent to the Laboratory of Wood Chemistry, Department of Forest Products and Institute of Forestry, to be fragmented in a hammer mill.

### 2.2. Tannin extraction

The material was extracted in a boiling flask under reflux for two hours having used a liquor/ bark ratio of 15:1. After extraction, the material was filtered under vacuum using a Büchner funnel. Each treatment was performed five times. The percentage of chemical products was calculated based on the dry weight of the barks. The treatments are schematized as follows:

- T1: Extraction with distilled water
- T2: Extraction with distilled water + 1% Na<sub>2</sub>CO<sub>2</sub>
- T3: Extraction with distilled water + 5% Na<sub>2</sub>CO<sub>2</sub>
- T4: Extraction with distilled water + 8% Na<sub>2</sub>CO<sub>2</sub>
- T5: Extraction with distilled water + 10% Na<sub>2</sub>CO<sub>2</sub>
- T6: Extraction with distilled water + 1% NaHSO,
- T7: Extraction with distilled water + 5% NaHSO,
- T8: Extraction with distilled water + 8% NaHSO<sub>3</sub>
- T9: Extraction with distilled water + 10% NaHSO<sub>3</sub>

### 2.3. Determination of extraction properties

For each treatment, the percentages of extractives and its properties were determined: percentage of condensed polyphenols as measured according to the Stiasny method (Stiasny Index – SI) and the UV method, content of tannins, content of non-tannins and pH value.

# 2.4. Chemical characterization of polyphenols (tannins)

The polyphenolic content was determined by the Stiasny reaction (Wissing, 1955; Lelis, 1995) and by the UV method (Roffael, 1976).

# 2.5. Determination of polyphenols by the reaction of Stiasny

After each extraction, an aliquot of 50 mL was added to a 250 mL-round-bottom flask. In addition, 5 mL of hydrochloric acid and 10 mL of formaldehyde were added. This material was then kept under reflux for 30 minutes and later filtered and washed with distilled water in a Büchner funnel of known weight. The residue (tannin) was then placed in a drying oven at a temperature of 105 + 3 °C until mass stabilization. The percentage of condensed tannin contained in the extracts (Stiasny Index – SI) was determined by calculating the ratio between tannin mass and the mass of total extractives extrapolated to 50 mL and the result converted to a percentage (Equation 1):

$$SI = \frac{\tan nin mass}{mass of total extractives} x 100$$
(1)

### 2.6. Determination of reactivity

The UV method is based on the Stiasny reaction, using a before and after aliquot of the filtrate to react with hydrochloric acid and formaldehyde (Roffael, 1976). For each sample, an absorbance reading in a spectrophotometer was performed, before and after the reaction, to verify reactivity. The readings were performed at a wavelength of 280 nm. The tannin reactivity was calculated coupled with the absorbance results from before and after the reaction.

# 2.7. Determination of tannin content and non-tannin content

To obtain the percentage of tannin in the bark, the Stiasny index was multiplied by the total amount of extractives and the result converted to a percentage. The difference between extractive content and tannin content provided the percentage of non-tannins.

### 2.8. pH determination

The pH of the solutions was obtained using a digital pH meter provided by QUIMIS. Measurements were conducted at room temperature and the value was registered after four minutes of electrode contact with the solution.

### 2.9. Statistical analysis

The design was completely randomized having five repetitions. The data referring to each test was subjected to variance analysis. Having rejected the null hypothesis, the F test was applied to the Scottknott test at a significance level of 5% for comparison between mean values.

# 3. RESULTS AND DISCUSSION

Content of polyphenols (SI), percentage of extractives, tannins and non-tannins for different treatments.

Table 1 presents the mean values of the different bark treatment for content of polyphenols (SI), % of extractives, tannins and non-tannins.

The Stiasny index (SI) represents the content of polyphenols (condensed tannins) existing in the extract. The results indicate that the distinct solvents used acted in an unequal manner in the solubility of polyphenol extracts. Generally, the treatments with varying proportions of sodium carbonate had higher values of Stiasny index over treatments with varying proportions of sodium bisulfite. The addition of sodium carbonate favored higher quantities of extractives and tannins (T2, T3, T4, T5).

The extractives content found in the treatment with water (24.84%) was superior to that found by Ferreira (2004), also working with the bark of Pinus oocarpa var. oocarpa. The values of Stiasny index (SI), percentage of extractives, percentage of tannins and non-tannins found in treatment T3 were slightly superior to those found by Ferreira (2004).

It has been observed that treatment T5 presented a high yield of tannins. Nevertheless, the percentage of non-tannins was notably high, too. High **Table 1.** Mean values of the Stiasny number (SI), % of extractives, % of tannins and % of non-tannins in the bark of *Pinus oocarpa* var. *oocarpa*.

**Tabela 1.** Valores médios do Número de Stiasny (NS), % de extrativos, % de taninos e % de não taninos na casca de *Pinus oocarpa* var. *oocarpa*.

Treatment	SI (%)	% Extractives	% Tannins	% Non-tannins
T1	65.56 <sup>c</sup>	24.84 <sup>F</sup>	16.24 <sup>F</sup>	8.60 <sup>B</sup>
T2	85.72 <sup>A</sup>	30.94 <sup>D</sup>	26.40 <sup>D</sup>	4.54 <sup>c</sup>
Т3	89.70 <sup>A</sup>	35.74 <sup>c</sup>	32.10 <sup>C</sup>	3.69 <sup>°</sup>
T4	90.54 <sup>A</sup>	43.92 <sup>B</sup>	39.74 <sup>A</sup>	4.18 <sup>c</sup>
T5	74.82 <sup>B</sup>	48.84 <sup>A</sup>	36.50 <sup>B</sup>	12.34 <sup>A</sup>
Т6	84.64 <sup>A</sup>	19.86 <sup>G</sup>	17.56 <sup>F</sup>	2.30 <sup>°</sup>
Τ7	72.28 <sup>B</sup>	26.70 <sup>E</sup>	19.28 <sup>E</sup>	7.42 <sup>B</sup>
Τ8	74.62 <sup>B</sup>	26.52 <sup>E</sup>	19.82 <sup>E</sup>	6.70 <sup>B</sup>
Т9	84.00 <sup>A</sup>	23.28 <sup>F</sup>	19.48 <sup>E</sup>	3.80 <sup>°</sup>

Means followed by the same letter, inside the same column, don't differ among themselves by Scott-knott to 5% of level of significance.T1: Extraction with distilled water,T2: Extraction with distilled water + 1% Na<sub>2</sub>CO<sub>3</sub>, T3: Extraction with distilled water + 5% Na<sub>2</sub>CO<sub>3</sub>, T4: Extraction with distilled water + 8% Na<sub>2</sub>CO<sub>3</sub>, T5: Extraction with distilled water + 10% Na<sub>2</sub>CO<sub>3</sub>, T6: Extraction with distilled water + 1% NaHSO<sub>3</sub>, T7: Extraction with distilled water + 5% NaHSO<sub>3</sub>, T8: Extraction with distilled water + 8% NaHSO<sub>3</sub>, T8: Extraction with distilled water + 8% NaHSO<sub>3</sub>, T8: Extraction with distilled water + 10% NaHSO<sub>3</sub>, T8: Extractind water + 10% NaHSO<sub>3</sub>, T8: Extraction wi

percentage of non-tannins may impair the use of the extract as an adhesive, mainly affecting its viscosity (Pizzi, 1994).

# 3.1. Polyphenol content by ultraviolet method (UV)

Table 2 presents the mean values of phenol content using the UV method.

The quantification of polyphenols through UV absorption can be considered more effective than the Stiasny method, because it also accounts for the polyphenols that react with formaldehyde and do not precipitate.

Through this method, it is observed that the mean values obtained for reactivity were high, indicating high reactivity between polyphenols (tannins) from the bark of Pinus oocarpa var oocarpa. Statistically, there were significant variations between the results obtained in the extraction with distilled water compared to other forms of extraction.

Ferreira (2004) obtained a tannin reactivity of 99.03% in the water extract of Pinus oocarpa var oocarpa with 5% sodium sulfite, this being similar to the value obtained in this study (94.51%). Souza (2006) obtained a tannin reactivity of 52.50% in a water extract of Eucalyptus pellita with 5% sodium sulfite, and Teodoro & Lelis (2003) acquired a tannin reactivity of 63.7% using only water, less than the result found in this study (85.32%).

**Table 2.** Mean values of polyphenol content from the bark of *Pinus oocarpa var. oocarpa* using the UV method.

**Tabela 2.** Valores médios do teor de polifenóis pelo método ultravioleta (UV) na casca de *Pinus oocarpa* var. *oocarpa*.

Treatment	Reactivity (UV) %
T1	85.32 <sup>B</sup>
T2	99.25 <sup>A</sup>
Т3	94.51 <sup>A</sup>
T4	96.90 <sup>A</sup>
T5	95.57 <sup>A</sup>
Т6	98.09 <sup>A</sup>
Τ7	99.21 <sup>A</sup>
Т8	99.50 <sup>A</sup>
Т9	98.29 <sup>A</sup>

Means followed by the same letter, inside the same column, don't differ among themselves by Scott-knott to 5% of level of significance.T1: Extraction with distilled water, T2: Extraction with distilled water + 1% Na<sub>2</sub>CO<sub>3</sub>, T3: Extraction with distilled water + 5% Na<sub>2</sub>CO<sub>3</sub>, T4: Extraction with distilled water + 8% Na<sub>2</sub>CO<sub>3</sub>, T5: Extraction with distilled water + 10% Na<sub>2</sub>CO<sub>3</sub>, T6: Extraction with distilled water + 1% NaHSO<sub>3</sub>, T7: Extraction with distilled water + 5% NaHSO<sub>3</sub>, T9: Extraction with distilled water + 1% NaHSO<sub>3</sub>, T9: Extraction with distilled water + 10% NaHSO<sub>3</sub>, T9: Extraction wateh wa

## 3.2. pH of extracts

Table 3 presents the mean values obtained for the pH of extracts.

The pH is of great importance in tannin reactivity, for only in an acidic pH can the condensation

**Table 3.** Mean pH levels of extract acquired from the bark of *Pinus oocarpa var. oocarpa*.

**Tabela 3.** Valores médios encontrados para o valor de pH dos extratos da casca de *Pinus oocarpa* var. *oocarpa*.

Treatment	pН
T1	3.01 <sup>F</sup>
Τ2	5.53 <sup>D</sup>
Т3	7.50 <sup>°</sup>
T4	8.06 <sup>B</sup>
T5	$8.74^{\text{A}}$
Τ6	3.20 <sup>F</sup>
Τ7	3.20 <sup>F</sup>
Τ8	3.52 <sup>E</sup>
Т9	3.32 <sup>E</sup>

Means followed by same letter, inside the same column, don't differ among themselves by Scott-knott to 5% of level of significance. T1: Extraction with distilled water, T2: Extraction with distilled water + 1% Na<sub>2</sub>CO<sub>3</sub>, T3: Extraction with distilled water + 5% Na<sub>2</sub>CO<sub>3</sub>, T4: Extraction with distilled water + 8% Na<sub>2</sub>CO<sub>3</sub>, T5: Extraction with distilled water + 10% Na<sub>2</sub>CO<sub>3</sub>, T6: Extraction with distilled water + 1% NaHSO<sub>3</sub>, T7: Extraction with distilled water + 8% NaHSO<sub>3</sub>, T9: Extraction with distilled water + 10% NaHSO<sub>3</sub>.

reaction between tannins and formaldehyde take place, resulting in the polymerization of the resin.

It has been observed that the addition of salts in the extraction process increased the pH of extracts, indicating that there were significant variations between the results. The results obtained in the treatment with pure water presented the lowest pH values, demonstrating the acidic nature of tannins in water extracts. Ferreira (2004) obtained a pH value in the water extract of Pinus oocarpa var. oocarpa of 3.35, similar to the value acquired in this study (3.01).

However, with the addition of higher concentrations of sodium bisulfite, there was an increase in the pH value, yet the extracts still presented an acidic nature. The higher mean pH values (above 7.0) occurred with the addition of sodium carbonate. Ferreira (2004) obtained a pH value of 7.21 in water extract with 5% sodium sulfite of Pinus oocarpa var. oocarpa, nearing the value acquired in this study (7.50).

### 4. CONCLUSIONS

The addition of sodium carbonate to the extraction process enhanced the solubilization of greater quantities of condensed tannins.

The addition of higher percentages of sodium bisulfite did not result in higher percentages of tannins.

Treatment with 8% sodium carbonate provided the highest yield of condensed tannins, underlining the importance of utilizing this specific salt concentration in the extraction process. However, the extracts must be evaluated according to other important bonding properties, including viscosity and gel time.

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